DAIKIN AMERICA, INC.

Daikin Advanced Lithium Ion Battery Technology – High Voltage Electrolyte

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Daikin Technical Center, Decatur, Alabama

DOE Annual Merit Review
June 13, 2019

Project ID: ES312

This presentation does not include proprietary, confidential or otherwise restricted information

Timeline

- Start Date: 10/1/16
- End Date: 3/31/20
- 66% Complete

Target and Barriers

- Performance – 300-1000 cycles at 4.6 V
- Failure mechanisms at high voltage

Budget

- Total - $1,826,895
  - DOE - $1,250,000
  - Daikin America - $576,895
- Expenditure of Gov't Funding
  - FY2017 524 K
  - FY2018 ~ 583 K (estimate)
  - FY2019 ~ 574 K (estimate)

Partners

- Interactions/Collaborations
  - PHI Minneapolis
  - University of Texas, Dallas
  - Evans Analytical Group

Project Objective: to develop a stable (300 – 1000 cycles), high-voltage (up to 4.6 V), and safe (self-extinguishing) formulated electrolyte.

- Performance Objective
  - Understand mechanisms for cell failure via electrolyte
  - Propose electrolyte solvent systems through DOE methods for high voltage battery systems. This includes optimization of additives
  - Optimize additive packages for increased cycle life

- Impact to DOE VT mission
  - Electrolytes which facilitate stable high voltage cycling of lithium ion batteries present a pathway to higher energy batteries.
  - Higher energy batteries enabled by simple material substitution not only positively impact gravimetric and volumetric energy density targets but also are beneficial towards DOE cost targets (wH/$)

200 mA-hr pouch cell

Composition baselines

1.2M $LiPF_6$ EC/EMC (2/8) + 1% PS
1.2M $LiPF_6$ EC/EMC/FE (2/6/2) + 1% PS
1.2M $LiPF_6$ FEC/EMC/FE (2/6/2) + 1% PS

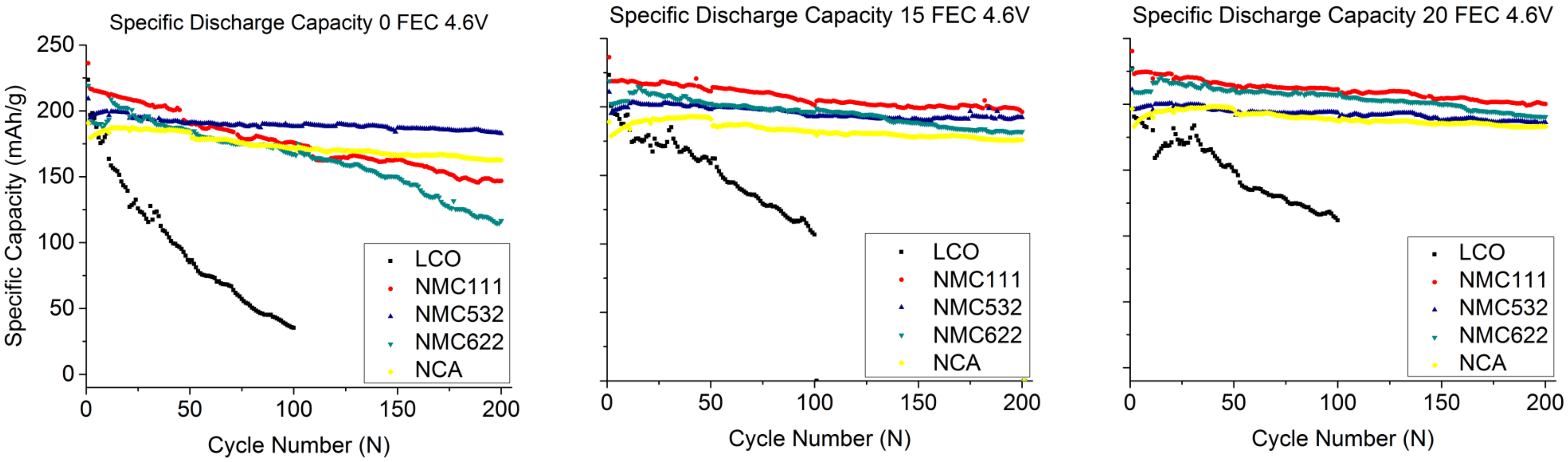
$LiCoO_2$ (LCO) cathode
$LiNi_{0.33}Mn_{0.33}Co_{0.33}O_2$ (NMC111) cathode
$LiNi_{0.5}Mn_{0.3}Co_{0.2}O_2$ (NMC532) cathode
$LiNi_{0.6}Mn_{0.2}Co_{0.2}O_2$ (NMC622) cathode
$LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$ (NCA) cathode

Graphite anode

Cells are anode limited and balanced for 4.4 V

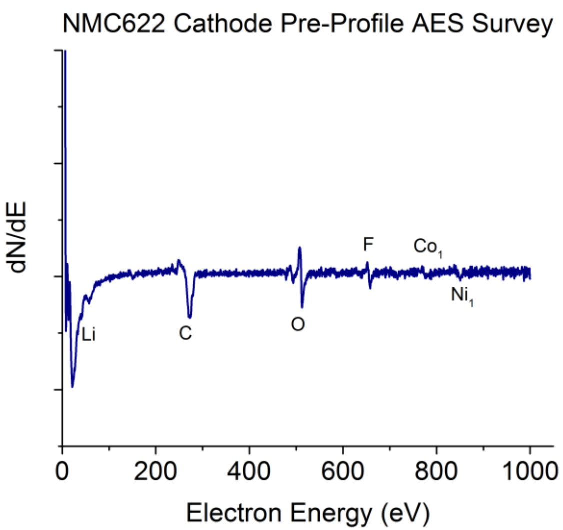
Upper Voltages
4.2, 4.5, 4.6 V

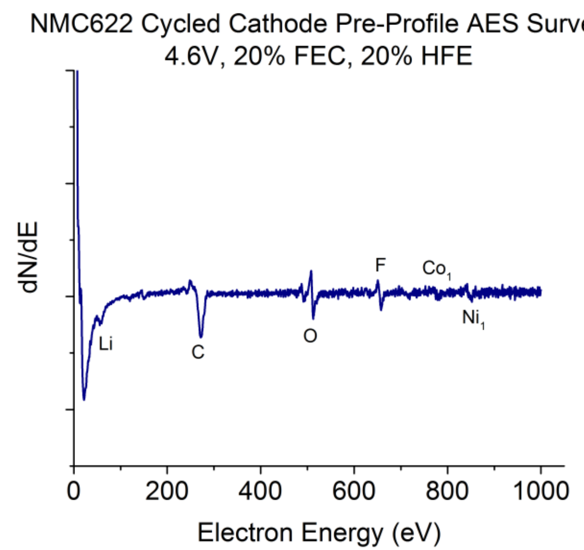
Cycle Performance to 4.6 V as a Function of [FEC] and Nickel Content



- Cycling experiments performed at r.t. at 0.7C with CC charge/CC discharge
- FEC is necessary at 4.6V, 15% (v/v) minimum

Film Composition and Thickness: **Milestones 2.1 and 2.2**



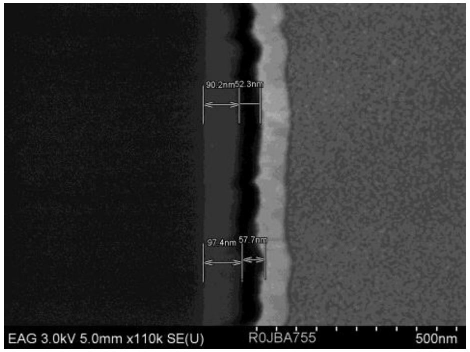


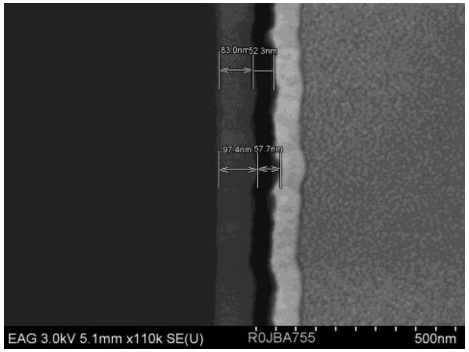
- Our approach to determine film thickness and elemental composition utilizes Auger Electron Spectroscopy (AES) and an Argon ion-gun sputter method

- However, a better sputter rate calibrant than SiO_2 is needed

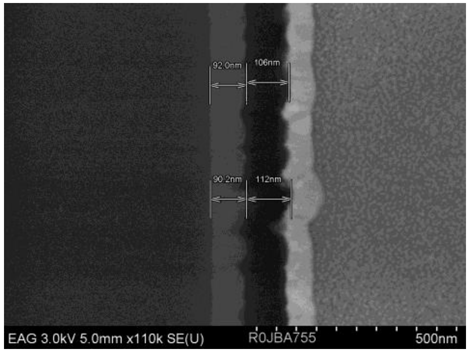
Film Composition and Thickness:
Milestones 2.1 and 2.2

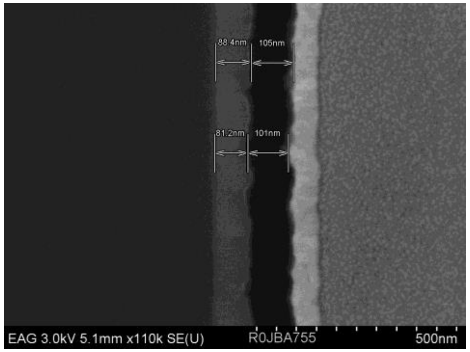
500 Å Film





1000 Å Film

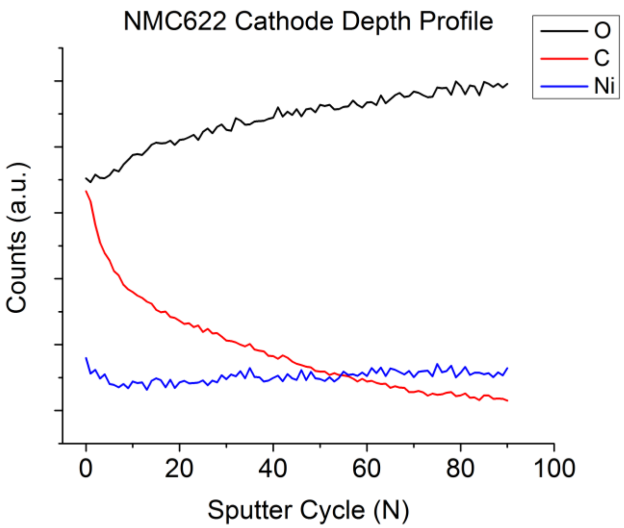


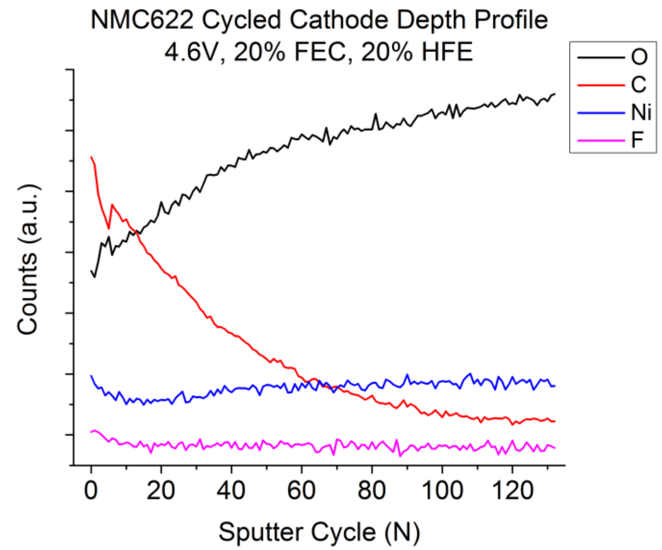


	Carbon (Å)	Aluminum (Å)
500 Å	**542**	**881**
1000 Å	**1080**	**851**

- Sputtered amorphous carbon films serve as the AES calibrant (≈ 1 nm/cycle)
- FIB-SEM Performed at Evans Analytical Group (Raleigh, NC)

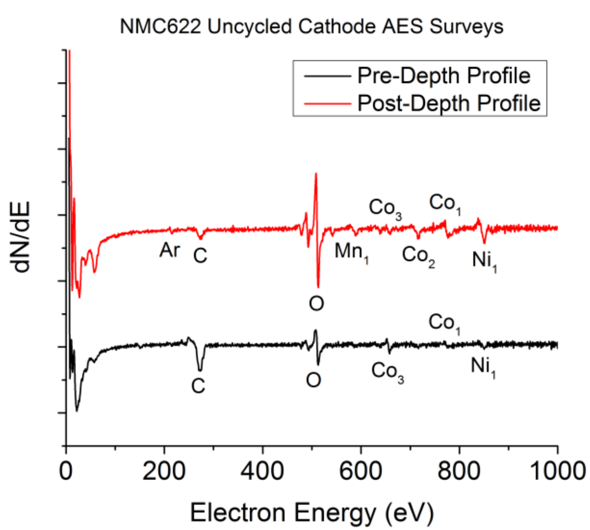
Film Composition and Thickness: **Milestones 2.1 and 2.2**

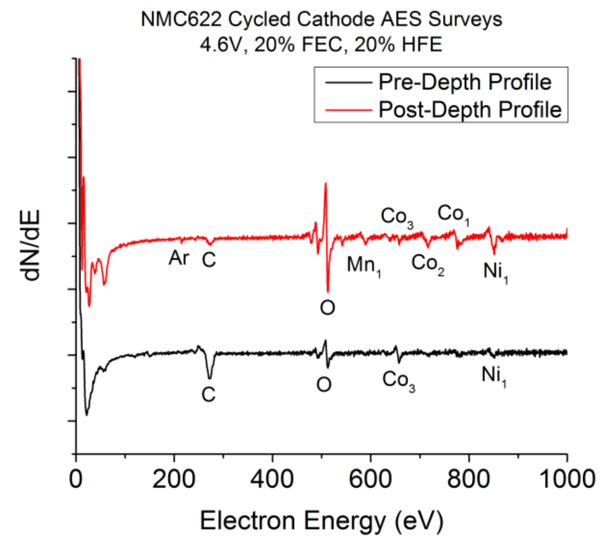




- On average, the cycled cathode requires 24-29 additional sputter cycles to diminish the carbon signal
- Film on NMC622 cathode (4.6V, 20% FEC, 20% HFE) ≈ 24-29 nm

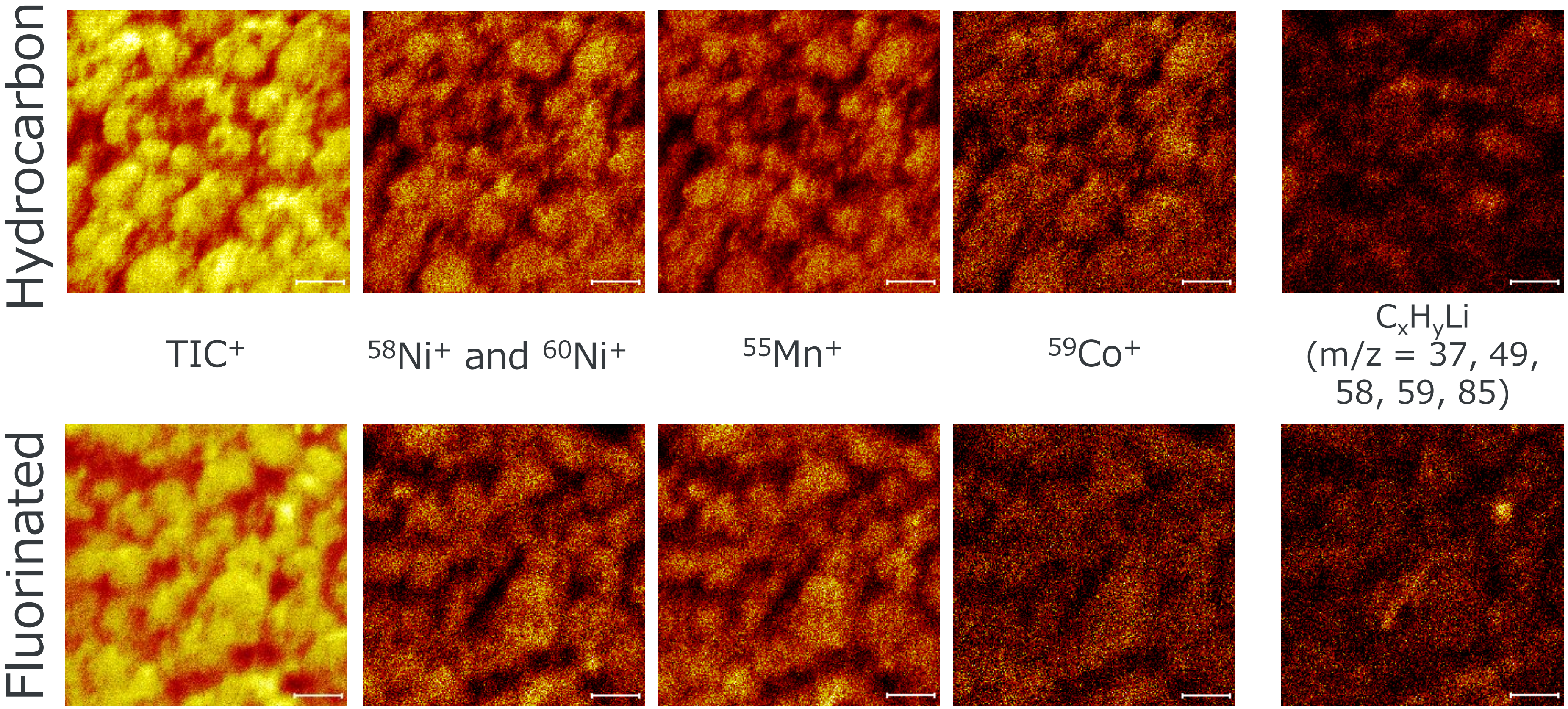
Film Composition and Thickness: **Milestones 2.1 and 2.2**





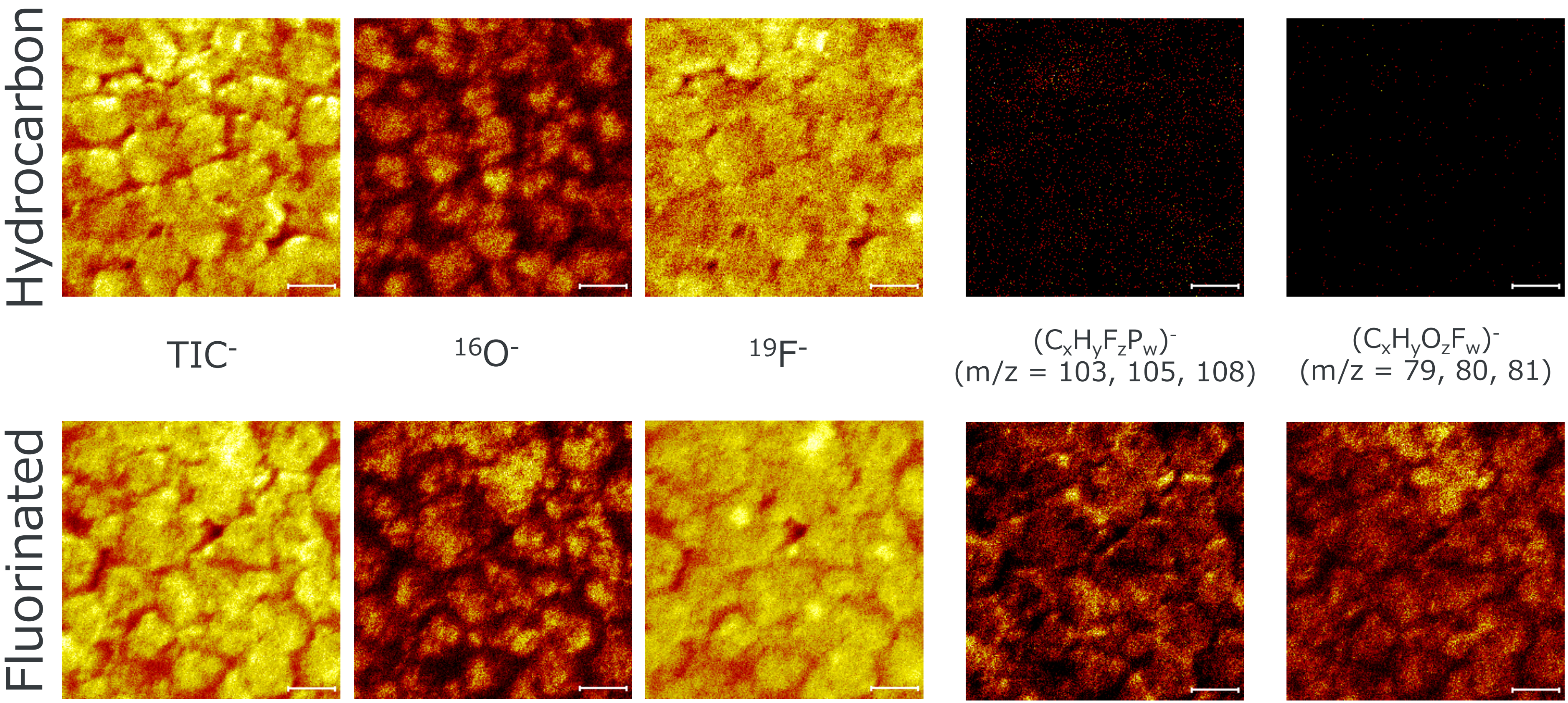
- Strong metal oxide signal post-depth profile
- Remnant carbon signal is from below surface particle depth
- Elemental information is inconclusive, chemical analysis is critical (TOF-SIMS)

NMC622 Cathode: 4.6V, Hydrocarbon vs. Fluorinated Electrolyte



- TOF-SIMS data was obtained in collaboration with Physical Electronics, USA (PHI)

NMC622 Cathode: 4.6V, Hydrocarbon vs. Fluorinated Electrolyte



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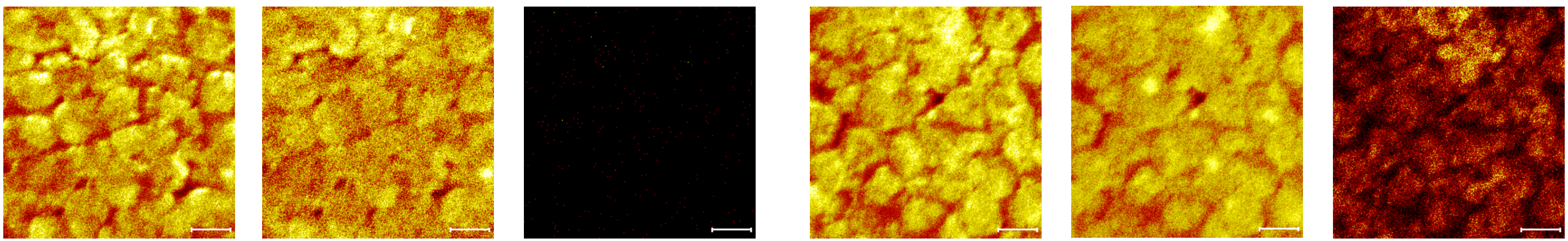
Film Composition and Thickness: **Milestones 2.1 and 2.2**

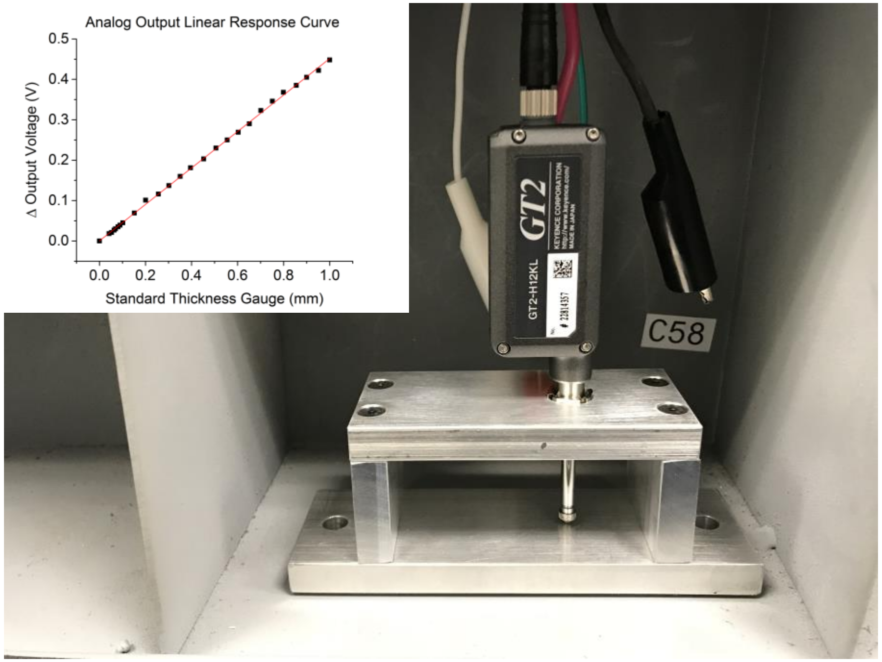
Hydrocarbon Electrolyte | Fluorinated Electrolyte

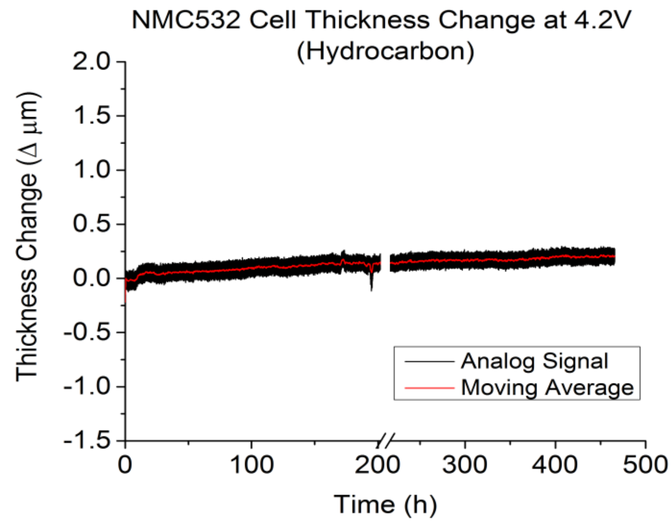


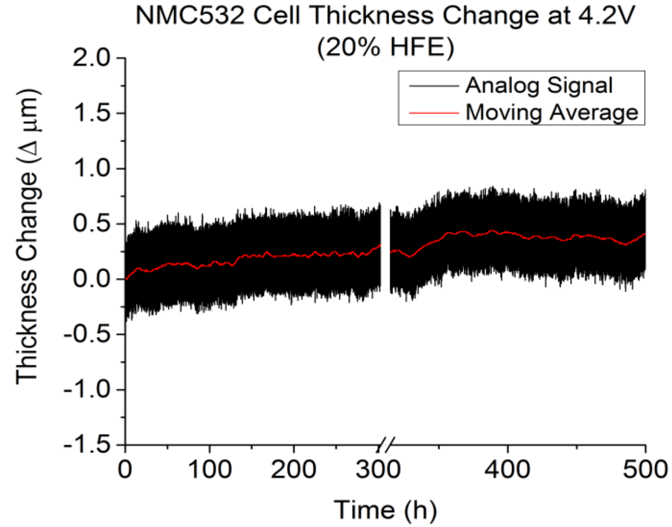
TIC$^-$ | $^{19}F^-$ | $(C_xH_yO_zF_w)^-$ | TIC$^-$ | $^{19}F^-$ | $(C_xH_yO_zF_w)^-$

- In summary: Fluorinated components of the electrolyte correlate to fluorinated organic fragments on the cathode
- Elementally, the SEI layer is identical regardless of electrolyte
- However, there is a significant chemical difference in the composition that is electrolyte-dependent

Battery Thickness vs. Time/Voltage







- Battery (non-gas) thickness measurements were obtainined using Keyence contact sensors
- Changes in the analog output signal are proportional to thickness changes (non-gas)
- Calibration curves of ΔV vs. thickness standards were generated
- Sensors have 1 mm accuracy and 0.1 µm resolution

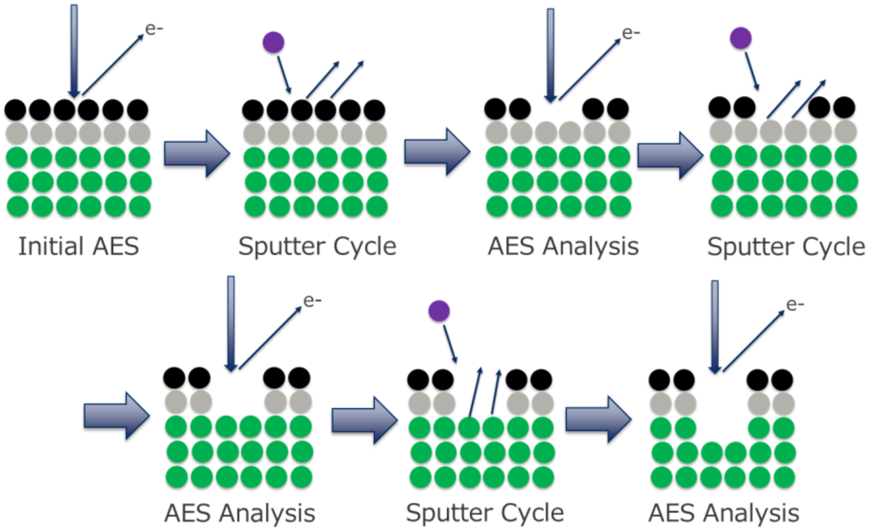
Summary & Acknowledgements

- Milestones in Year 2 are primarily centered around physical analysis of the films formed on the electrodes by introduction of fluorinated additives in the electrolyte
- Using the carbon films to determine thickness as a function of sputtering time, a film thickness of 24-29 nm was observed for electrodes exposed to fluorinated electrolyte.
- TOF-SIMS analysis of the cycled cathodes suggests the presence of hydrocarbon-fluorocarbon film on the electrodes when a fluorinated electrolyte is used
- Electrochemical performance has been completed for all chemistries which were proposed. NCA cathodes also show stable cycle life at 4.6 V
- A plan to submit interim cells has been established. It includes 30 NMC532/Graphite cells with to-date best practice fluorinated electrolyte.

Daikin gratefully acknowledges funding from DOE Vehicle Technologies Office (Tien Duong) and TARDEC (Yi Ding)

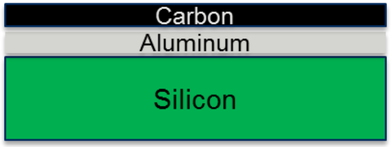
Technical Back Up Slides

Surface Techniques for Bulk Analysis



Alternating sequence of Argon sputtering and AES

Thickness Standard Expts



AES beam:
- 3kV
- ~200nA

AES Multiplex:
- Monitor C, Al, Si, and O intensity
- Focus on C, Al, and Si

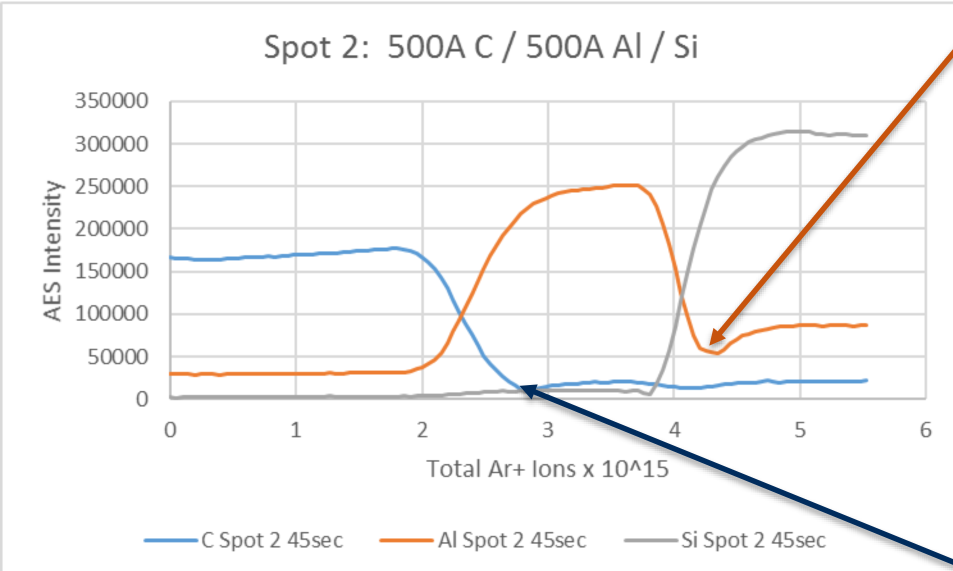
Ar^+ ion beam:
- 3keV
- ~180nA
- 1mm x 1mm raster

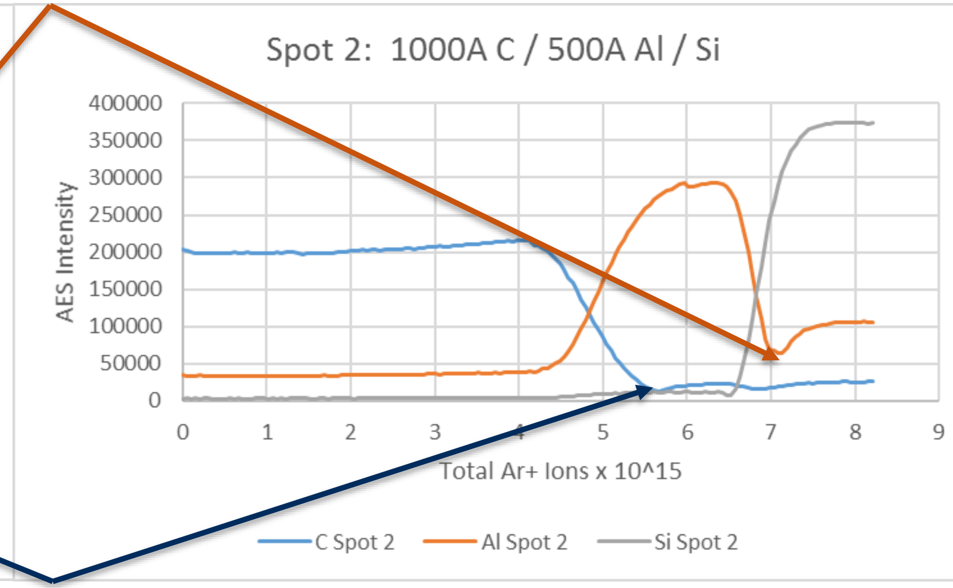
Ion beam dwell (time per sputter cycle):
- 45 sec (all other spots on both samples)
- 60 sec (Spot 1, 500Å C)

Samples:
- 500Å C / 1000Å Al / Si wafer
- 1000Å C / 1000Å Al / Si wafer
- 3 spots per sample are measured

Methodology to Determine Film Thickness

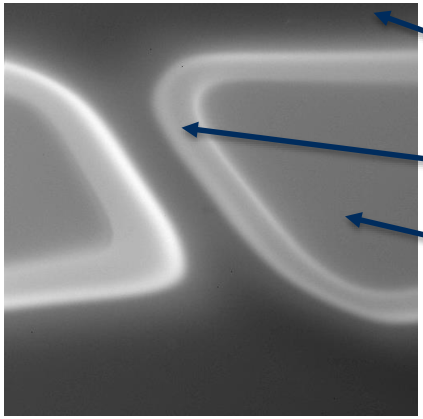
Aluminum completely removed



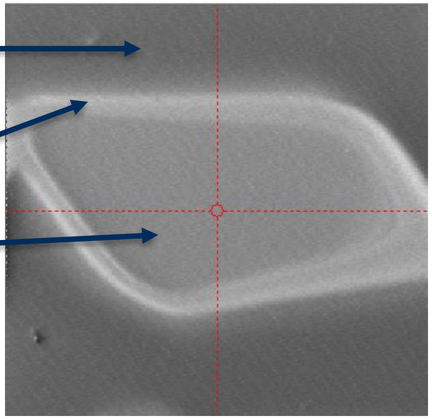


Carbon completely removed

500Å C/Spot 2,3



1000Å C/Spot 2



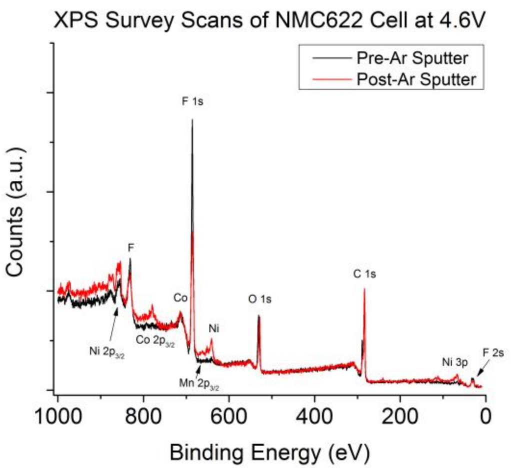
Carbon

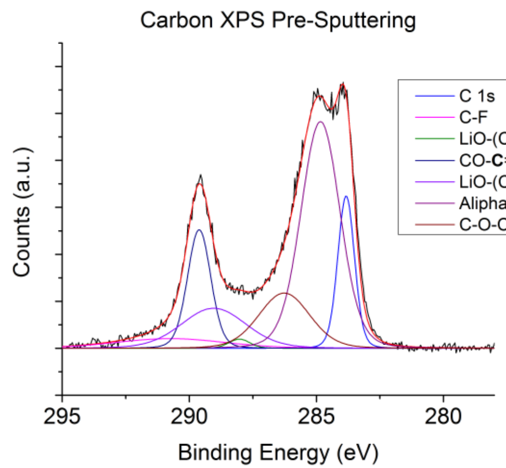
Aluminum

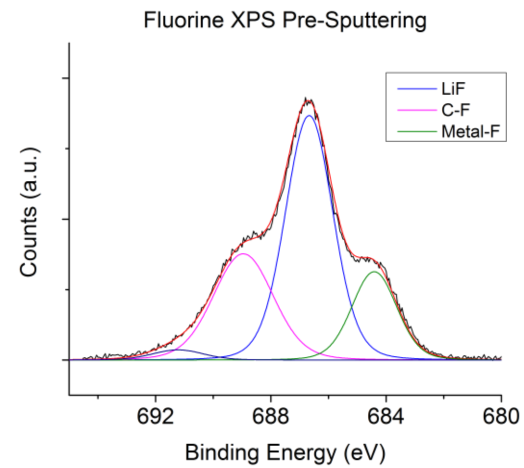
Silicon

Red crosshair indicates the electron beam impact position where the AES measurements were made.

Film Composition and Thickness: **Milestones 2.1 and 2.2**







- XPS spectra of tested NMC622 cathode (4.6V, fluorinated electrolyte, 200 cycles). Survey before and after a short sputter cycle (left), Carbon 1s (middle), and Fluorine 1s (right) fitted spectra are depicted[1]
- Pre-sputter multiplex data is representative of surface chemical species. Investigation of changes as a function of depth is ongoing

1) Shulz, N. et. al, *J. Electrochem. Soc.*, **2018**, *165(5)*, A819-A832